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CO2-PRODUCTION BY IMPACT IN CARBONATES ?: AN ATEM- AND STABLE ISOTOPE (C,O) STUDY;

I. Martinez, P. Agrinier, F. Guyot, Ph. Ildefonse, M. Javoy, U. Schärer, Univ. Paris 7, 2 place Jussieu, 75251 Paris cedex 05, France and U. Hornemann, A. Deutsch, Inst. für Planetologie, Univ. Münster, Wilh. Klemm Str. 10, D-4400 Münster, Germany.

Carbonates may have been a common target for large impacts on the Earth and possible related CO_2 outgassing would have important consequences for the composition of the atmosphere. To estimate volatile release during such impacts, isotopic ratios ($^{13}C/^{12}C$ and $^{18}O/^{16}O$) were determined on highly shocked carbonate samples in combination with SEM and analytical transmission electron microscopy (ATEM) investigations. The study was performed on both naturally and experimentally shocked rocks, i.e. 50-60 GPa shocked limestone-dolomite fragments from the Haughton impact crater (Canada), and carbonates shocked in shock recovery experiments such as described in [1]. For the experiments, unshocked carbonates consisting of mixture of dolomite and calcite from the Haughton area were used. Naturally shocked samples were collected in the polymict breccia [2] near the center of the Haughton crater (Anomaly Hill [3]).

Previous shock experiments [4,5] on limestones have suggested that for high pressures of about 60 GPa, roughly 70% of CO_2 should be volatilized. If CO_2 is released to such a large degree, strong isotopic effects should be registred, because CO_2 is enriched in ^{13}C and ^{18}O and consequently, residual carbonates are depleted in these isotopes if classical thermal decarbonation occurs [6]). In addition, this isotopic effect should be correlated with CaO,MgO enrichment in the residual solid. The theoretical Rayleigh model curve for such progressive loss of CO_2 is shown in Fig. 1. In our samples from Haughton, i.e. 30 highly shocked clasts (full squares in Fig. 1), carbonates represent between 0.5 to 10 wt% of the rock. As shown in Fig. 1, ^{13}C is enriched in most of the samples instead of being depleted as to expect from the classical decarbonation model. Values for $\delta^{13}C$ range up to +9‰, relative to about -3‰ in the unshocked references samples (open squares), and relative to values of about -1‰ measured in lacustrian sediments that formed in the crater-lake (open triangles). On the other hand, the very same carbonate fractions are systematically depleted in ^{18}O with $\delta^{18}O$ ranging between +14‰ and +22‰ (Fig. 1). In contrast to these naturally shocked samples, carbonates shocked experimentally to the same pressure conditions reveal largely unchanged isotopic composition ($\delta^{13}C$= -3‰, $\delta^{18}O$ = 25‰, Fig. 1 open circles) compared to the unshocked aliquots. Moreover, the experimentally shocked samples still consist exclusively of calcite and dolomite yielding the same relative volumes of CO_2-gas such as obtained from the unshocked equivalents.

Experimentally shocked samples. X-ray diffraction spectra on the 60 GPa shocked carbonates confirm that only calcite and dolomite are present after the experiment; not the slightest evidence for the existence of CaO or MgO is observed. X-ray diffraction lines of dolomite and calcite are broadened due either to large plastic deformation within the crystals, mosaic textures, or disordering of Mg and Ca in the lattice. SEM documents that after the shock, both calcite and dolomite crystals are highly fracturated relative to individual grains in the unshocked samples but again, no major chemical transformation was observed. Electron diffraction patterns (TEM) substantiate important crystallographic disorientations within single crystals of calcite and dolomite. These results are in good agreement with the stable isotope data from these samples (Fig. 1), which do not yield any evidences for decarbonation.

Naturally shocked samples. SEM studies reveal that carbonate crystals in the 50-60 GPa shocked fragments from Haughton occur essentially along cavity walls (bubbles, cracks). These 10-100 μm-size calcite and dolomite crystals lie adjacent to either a pure SiO_2 phase or a silica-rich phase containing minor amounts of Al, K, Mg, Na, and Ca. Another observation is that the carbonates have reacted with the SiO_2 phases producing domains that have the chemical composition of aegirine-augite (Ca-Mg pyroxene), larnite (Ca_2SiO_4), or domains with a Si-Al-Ca-Mg chemistry which does not correspond to any distinct mineral. In thin-sections, these domains are essentially isotropic, and no individual crystals can be distinguished. An ATEM

study was performed on these samples to obtain a better resolution for images ($\approx$ 4Å) and information on the crystallographic state of the shock produced phases. It shows that carbonates are present either as very small crystals (< 400 nm large) or bigger crystals (> 500 nm) which contain planar defects essentially in dolomite. The ATEM also corroborates the existence of strong shock-metamorphic reactions between silicates and carbonates at high temperatures. Some glasses, in contact with small crystals of calcite, are characterized by a garnet-like chemical composition (($(Ca,Mg)_3Al_2Si_3O_{12}$) representing pyrope-grossular glass. Other types of glass show a Ca-Mg pyroxenitic composition or SiO_2 composition with minor amounts of Mg, Al, and K. In association with calcite and dolomite in the highly shocked Haughton samples, other types of 2000 nm large crystals are produced by these reactions: β-Ca_2SiO_4 (larnite), typical for temperature above 700°C and generally sensitive to alteration, and unreverted pigeonite (Ca-poor monoclinic pyroxene). Such pigeonite is generally reverted to an orthorombic pyroxene by cooling below 1000° C and therefore, the unreverted form is typical for fast cooling conditions. This observation, together with the presence of larnite and glass, are strong evidences in favour of very rapid quenching after the shock.

From our observations, it appears that the classical decarbonation reaction ($CaMg(CO_3)_2 \rightarrow$ $CaO + MgO + 2CO_2$) does not occur on a large scale either in the naturally or experimentally, 50-60 GPa shocked carbonates. Concerning the experiments, holes of different configurations were drilled in the ARMCO-steel container in order to facilitate CO_2 escape through the container however, even these experiments did not yield any evidence for decarbonation reactions either on calcite or dolomite. The absence of this reaction was already suspected by field and petrographic observations in the Haughton crater, where no highly shocked carbonates or CaO-MgO reaction products could be identified. Moreover, the occurence of this type of fragment is limited to the center of the crater, representing a very minor part of the shocked rocks. The ^{13}C and [18]O effects observed here are probably related to post-shock temperatures. In consequence, the ^{13}C systematics of these samples can be interpreted as the back-reaction with CaO, MgO or calcium silicates of small amounts of ^{13}C enriched CO_2 previously produced by partial, and very limited decarbonation. On the other hand, the [18]O depletion in these carbonates can be ascribed to the observed reactions with liquid SiO_2 phases ($\delta^{18}O \approx +10‰$) which penetrate these fragments (see above).

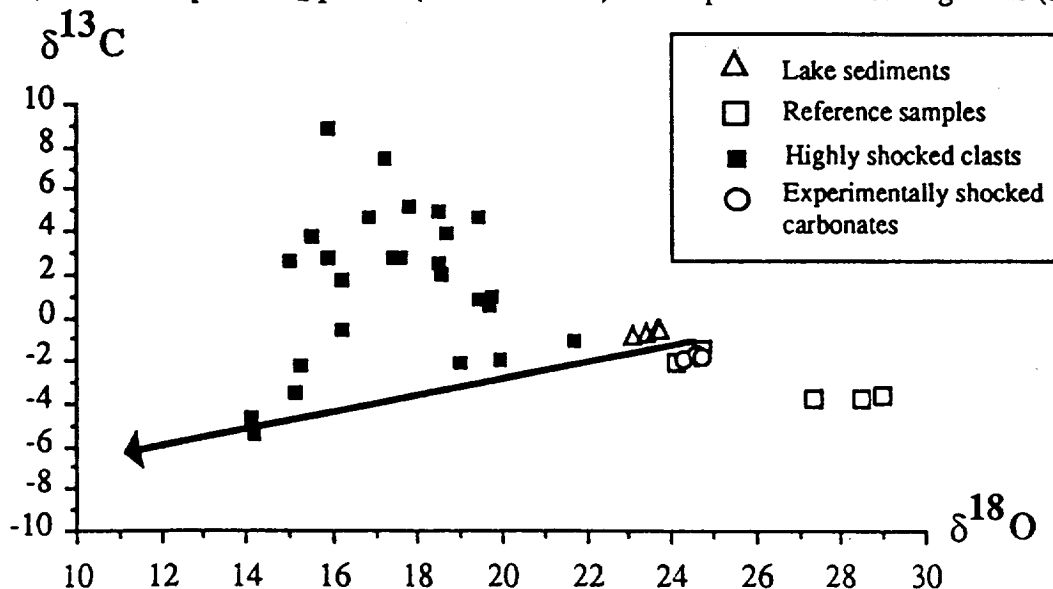Fig 1: δ13C vs δ18O. The line represents a degassing of CO2 according the Rayleigh law, with α carbon=1.0022 and α oxygen= 1.0060

[1] Redeker H.J. and Stöffler D. (1988) *Meteoritics* 23,185. [2] Müller W.F. and Hornemann U. (1969) *Earth Planet. Sci. Lett.*, 7, 251. [3] Pohl J. et al. (1988) *Meteoritics* 23,185. [4] Lange M.A. and Ahrens T.J. (1986) *Earth Planet. Sci. Lett.*, 77, 409. [5] Tyburczy J.A. and Ahrens T.J. (1986) *JGR*, 91, 4730. [6] Valley J.W. (1986) Rev. in mineralogy, 16, 445.